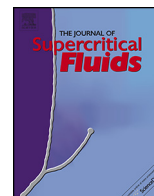




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# Supercritical water oxidation with hydrothermal flame as internal heat source: Efficient and clean energy production from waste

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### ABSTRACT

Supercritical water oxidation (SCWO) has the potential to be considered a clean energy generation process, as the process effluent is a high temperature, high pressure stream with a high enthalpy content that can be converted to heat and shaft work. In this work the state of the art of SCWO has been reviewed, focusing on energy production. For the description of thermodynamic and transport properties, there are some methods recommended for pure substances, but the applicability of those methods for mixtures at supercritical state is yet not clear. Most of the work found in literature use cubic equations of state and linear mixing rules. The design of reactors has evolved in order to reduce the drawbacks of corrosion and salt deposition, in general, through the dilution of reaction products. In order to make the process profitable energetically different strategies must be used to keep the products at the highest temperature without compromising the safety, and the hydrothermal flames if correctly stabilized are a good choice. Reactors and reaction systems able to process feeds consisting of suspension with high inorganic contents without diluting the effluent reducing its temperature must be developed. On the other hand, the systems of energy recovery must be improved, especially the expanders, in order to recover the pressure work as well as the thermal energy. Modeling tools can help in both aspects. But for developing good models a good comprehension of thermal and transport properties of mixtures at supercritical state, as well as oxidation kinetics under that condition are essential data that must be further investigated in order to find energetically efficient processes.

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## 1. Introduction

Supercritical water oxidation is a process well-known for its environmental applications. Although its industrial development progresses slowly, this year several industrial plants for chemical weapons and sludge treatment are under construction [1]. Due to these development efforts, the limitations and challenges in the implementation of SCWO processes are also well-known, including the control of corrosion and salt precipitation processes [2–4]. Another well-known challenge of SCWO is the energy requirement, which can be high, particularly if simple plug-flow tubular reactors are used, since these designs require preheating of the influent up to supercritical temperatures. However, under appropriate operating conditions, the SCWO process can be energetically self-sufficient

or even produce a net excess of energy [5,6]. The correct use of the energy produced by the oxidation is a crucial step in order to make SCWO processes economically viable.

The main industrial development has been associated to sludge treatment by tubular reactors [1,7]. Conventional reactors are thin tubes about 100 m long, with evident plugging problems from solid precipitation. In practice, industrial plants work with two reactors, one under operation and the other undertaking the cleaning of deposited solids. In some applications the change of the reactors takes over 30 min. Furthermore, cleaning is a highly energy and time consuming step. Although the reactor effluent energy can be recovered by a Rankine Cycle, the process is still highly demanding. Additionally, oxygen is the most usual oxidant to reduce the energy consumption of the air compressor. The energy associated to the compression could be recovered if the work from effluent depressurization could be retrieved by a turbine.

Another reactor under industrial development is the transpiring wall reactor [8]. The transpiring flow allows a continuous clean water flow that protects the reactor against corrosion and plugging

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**Nomenclature**

$P$	pressure (MPa)
$T$	temperature (K)
$c_p$	constant pressure heat capacity ( $\text{J kg}^{-1} \text{K}^{-1}$ )

**Abbreviations**

CFD	computational fluid dynamics
EoS	equation of state
PR	Peng–Robinson equation of state
IPA	isopropyl alcohol
NIST	National Institute of Standards and Technology
PSRK	predictive Soave–Redlich–Kwong EoS
RKS	Redlich–Kwong–Soave EoS
SCW	supercritical water
SCWO	supercritical water oxidation
SR-Polar	Schwartzentruber–Renon EoS
TOC	total organic carbon
TWR	transpiring wall reactor
VTPR	volume translated Peng–Robinson EoS

but dilutes the effluent and reduces its temperature, so the heat recovery is reduced.

The cooled wall reactor developed at Valladolid University is the only reactor prototype currently in operation with hydrothermal flame as internal heat source that produces a reduced liquid effluent with dissolved solids and a high-pressure and high-temperature effluent [9,10]. It has been operated for more than 3 years with liquid feeds. With the appropriate heat integration, the heat recovery from the effluent would allow reach a net energy efficiency of 27%.

Hydrothermal flames were first presented in 1988 by Prof. Franck and Schilling [11]. At that time, they were considered a scientific curiosity due to the extremely high pressure (near 100 MPa) and the high concentration of methane used in the experiment. These are flames produced in aqueous environments at supercritical conditions [12]. Such flames are formed when fuel and oxidant streams are mixed at conditions that enable autoignition, producing an oxidation process at adequate temperature and rate to produce a luminous flame. The role of the high pressure is to reduce the temperature needed for autoignition, and nowadays the understanding of the phenomenon allows controlling hydrothermal flames at temperatures around 400–500 °C. Oxidizing at these temperatures permits reducing the concentration of combustible material in the feed. Besides, the operation under hydrothermal flames allows total oxidation of the wastes within milliseconds residence times, which opens the possibility of developing small combustors to produce high-pressure gas/vapor streams. The application of hydrothermal flames opens a wide field for the production of energy from wastes.

Research is still needed to improve the reactors development in order to operate with waste suspensions for energy production and reducing the reactor cost. It is also necessary to progress in the effluent energy recovery, not only the thermal energy but also the work. The improvement of this energy recovery will open the opportunity to operate with air as an oxidant and in small scale plants. The knowledge and experience obtained from SCWO environmental applications can foster the development of SCWO energy generation processes. The main differences are the operation with higher organics concentration (fuel) that needs to be taken into account along with the physical properties of the mixture. Also, the hydrothermal flame kinetic studies and modeling are essential to improve the understanding of the process.

In this manuscript a review of the research in the use of SCWO for energy production to date is presented as well as the research needs for the future development of this process.

**2. Supercritical water as reaction media****2.1. Properties**

Supercritical water (SCW) acts as a non-polar dense gas and its solvation properties resemble those of a low-polarity organic solvent. SCW shows complete miscibility with “permanent” gases, such as nitrogen, oxygen, and carbon dioxide, while inorganic salts are almost insoluble in it [13]. It presents also high diffusivities and low viscosities. Concerning the modeling of industrial SCWO processes working with high organic material concentrations, interest is focused on knowing the properties of aqueous mixtures.

When energy balances are necessary, a good estimation of the thermophysical properties is required, and when computational fluid dynamics (CFD) modeling is performed a good knowledge of the transport properties is also needed. With the scaling up of processes and the interest in their heat integration, models taking into account mass and energy balances were developed [5,6,14,15]. To obtain accurate results from this kind of models, precise values of densities, enthalpies, and heat capacities are needed, for both water and aqueous mixtures. Calculating the properties of aqueous systems in the surroundings of the critical point of water is a difficult task. Conventional cubic equations of state (EoS) are not very accurate in this region, although the Peng–Robinson EoS with the volume translation correction (VTPR EoS) [16,17] is able to reproduce densities of the water–air system quite accurately and to reproduce the behavior of real SCWO reactors (e.g. [18,19]). Anikeev et al. [20] also used a cubic EoS, the Redlich–Kwong–Soave (RKS) [21], to describe the dehydration of 2-propanol in supercritical water. Kutney et al. [22,23] developed a hard-sphere volume-translated van der Waals EoS able to calculate thermodynamic properties of several substances involved in the SCWO and their mixtures in conditions up to 40 MPa and 500 °C. Densities and residual properties can be predicted with average errors of 5% and 7%, respectively. The presence of salts in the mixture modifies the liquid–vapor equilibrium and more complicated EoS are necessary. Anderko et al. [24] summarized several EoS developed for modeling high-temperature and supercritical electrolyte–aqueous systems, including the Anderko–Pitzer EoS [25]. It is a comprehensive EoS for representing liquid–vapor and solid–liquid equilibria as well as volumetric properties. In the Anderko–Pitzer model, the EoS parameters were fitted to an extensive amount of experimental data of the water–NaCl system in the temperature range from 573 to 773 K and to a more limited amount of data above 773 K and pressures up to 500 MPa. In both temperature regions, the EoS reproduces the liquid–vapor equilibrium, volumetric properties, and solubility of solid NaCl within experimental uncertainty. An extensive list of salt–water systems correctly described by extensions of the Anderko–Pitzer EoS can be found in Bermejo and Cocero [7]. Even though there are several models for thermodynamic properties calculation, most of the works available in literature estimate mixture properties using cubic EoS or averaging tabulated reference properties of the pure components, as shown in Table 1.

The development of more complex reactor designs, such as the reverse flow reactor vessel or the transpiring wall reactor, and the awareness of the importance of the reagents mixing [40] have opened the way to more complicated models using CFD tools [18,33,39] to accurately describe the flow pattern inside the reactor. With this objective, the momentum balance must be solved and accurate values of the transport properties are needed.

**Table 1**

Thermodynamic models used for calculations of density and heat capacity in SCWO mixtures.

Work	Density	$C_p$
Anikeev et al. [20]	RKS	–
Bermejo et al. [26]	VTPR	IM (NIST) <sup>a</sup>
Chen et al. [27]	Pure water	Pure water
Donatini et al. [15]	PSRK	–
Dutournié et al. [28]	Pure water	Pure water
Lavric et al. [6]	PR	PR
Leybros et al. [29]	IM (VTPR) <sup>a</sup>	IM (VTPR) <sup>a</sup>
Lieball [18]	IM (VTPR) <sup>a</sup>	IM (VTPR) <sup>a</sup>
Moussière et al. [30]	Ideal Mixing	Ideal Mixing
Moussière et al. [31]	IM (NIST) <sup>a</sup>	IM (NIST) <sup>a</sup>
Narayanan et al. [32]	IM (VTPR) <sup>a</sup>	IM (VTPR) <sup>a</sup>
Oh et al. [33]	IM (SR-Polar, NIST) <sup>a,b</sup>	IM (SR-Polar, NIST) <sup>a,b</sup>
Queiroz et al. [34]	VTPR	PR
Queiroz et al. [35]	VTPR	PR
Sierra-Pallares et al. [36]	VTPR	VTPR
Vielcazals et al. [37]	Pure water	Pure water
Zhou et al. [38]	IM (NIST) <sup>a</sup>	IM (NIST) <sup>a</sup>
Zhou et al. [39]	SUPERTRAPP	SUPERTRAPP

<sup>a</sup> IM stands for ideal mixture. The property of each pure component is calculated by the method inside parenthesis.

<sup>b</sup> NIST for water; SR-Polar for other species.

**Viscosity.** The prediction equation described by Huber et al. [41] is recommended by the International Association for Properties of Water and Steam (IAPWS) [42] for calculating water viscosity. This equation computes viscosity as a function of reduced temperature and density and can be applied for pressures up to 1000 MPa and temperatures up to 900 °C in some conditions, with uncertainty of 3%. Poling et al. [43] discuss three methods of viscosity estimation for gas mixtures at high pressures: Lucas [44], Chung et al. [45] and TRAPP method [46,47]. The three methods yield similar results, but TRAPP procedure can be extended to liquid region.

**Thermal conductivity.** The formulation recommended by IAPWS for the calculation of the thermal conductivity of water as a function of temperature and density is presented by Huber et al. [48]. The range of application is up to 1000 MPa and up to 900 °C, and the uncertainties at the usual conditions of SCWO are between 4% and 6% [49]. Poling et al. [43] presented also three methods to estimate thermal conductivity of high-pressure gas mixtures (Stiel and Thodos [50], Chung et al. [45] and TRAPP [46,47]), all of them with errors averaging about 5–7%. However, the database used for testing is small and does not contain polar fluid mixtures.

**Diffusion coefficient.** Most of the research work done in the field of diffusion coefficients in supercritical fluids is focused on extraction processes and chromatography. Hence, the experimental data and correlations available for diffusivities come mainly from

non-aqueous systems, where the solvent is an organic (e.g. ethylene, propane, hexane) or CO<sub>2</sub> [51,52]. For aqueous systems, diffusivity data near the critical point are much more limited. Kutney [51] studied a large list of methods for the prediction of self-diffusion coefficients for the system acetone-water and recommended two methods: the method of Mathur and Thodos [53], based on Kinetic Theory; and the modified method called Tracer Liu–Silva–Macedo [54], based on Hard-Sphere Theory. Poling et al. [43] recommend the simple correlation of He and Yu [55] for binary diffusion coefficients, while Svishchev and Plugatyr [56] used molecular dynamics simulation for modeling the SCWO of *o*-dichlorobenzene. In practice, the industrial and pilot SCWO plants work with flow rates that lead to turbulent flow regime, where the diffusive transport is negligible if compared to the “turbulent diffusion” result of fluctuations in the advective transport. Thus, detailed models for the laminar diffusion coefficient are not necessary.

Table 2 shows the approaches used in some works concerning CFD simulation of SCWO reactors.

## 2.2. Kinetics

The development on the SCWO process as waste elimination technology has impulsed the quantitative understanding of the SCWO reaction rates of different types of organic species at the lower temperatures of 450–500 °C [57]. The focus of these kinetic studies has typically been on model compounds rather than on actual waste. These compounds have been chosen because they contain key functional groups of importance and/or represent the rate limiting step in the breakdown of a range of complex waste species [58]. Considering only homogeneous reactions without catalysts, extensive data on SCWO kinetics have been reported for a number of model compounds [57–62].

In the field of complex chemistry, Webley and Tester [63] did the pioneering work by adapting a gas-phase combustion mechanism with 56 reversible elementary reactions to SCWO conditions. They found that the model predicts methanol oxidation to be much more faster than it was observed experimentally, and this mismatch led them, and others, to speculate on how SCW might be influencing the kinetics. More recent work in the field, however, which consistently finds good agreement between experimental and predicted kinetics, suggests that the chief reason for this earlier discrepancy was the authors' use of a value for the rate constant for the reaction  $\text{H}_2\text{O}_2 \leftrightarrow \text{OH} + \text{OH}$  that was about two orders of magnitude too high. This high value appeared to result from Webley and Tester erroneously extrapolating the low-pressure limit rate constant to the high-pressure encountered in SCWO [64]. Dagaut et al. [65] used a mechanism derived from that published for the atmospheric

**Table 2**

Methods of estimation of transport properties used in CFD models of SCWO.

Work	Viscosity	Thermal cond.	Diffusivity
Bermejo et al. [26]	IM (NIST) <sup>a</sup>	IM (NIST) <sup>a</sup>	–
Chen et al. [27]	Pure water	Pure water	Pure water
Dutournié et al. [28]	Pure water	Pure water	–
Leybros et al. [29]	Ideal mixing	Ideal mixing	–
Lieball [18]	IM (Chung et al.) <sup>a</sup>	IM (Chung et al.) <sup>a</sup>	Liu & Macedo, He <sup>c</sup>
Moussière et al. [30]	Ideal mixing	Ideal mixing	–
Moussière et al. [31]	IM (NIST) <sup>a</sup>	IM (NIST) <sup>a</sup>	–
Narayanan et al. [32]	IM (Chung et al.) <sup>a</sup>	IM (Chung et al.) <sup>a</sup>	He
Oh et al. [33]	IM (SR-Polar, NIST) <sup>a,b</sup>	IM (SR-Polar, NIST) <sup>a,b</sup>	–
Queiroz et al. [35]	IM (NIST) <sup>a</sup>	TRAPP	–
Sierra-Pallares et al. [36]	Lucas et al.	Lucas et al.	Mathur & Thodos
Zhou et al. [38]	IM (NIST) <sup>a</sup>	IM (NIST) <sup>a</sup>	–
Zhou et al. [39]	SUPERTRAPP	SUPERTRAPP	–

<sup>a</sup> IM stands for ideal mixing. The property of pure component is calculated by the method inside parenthesis.

<sup>b</sup> NIST for water; SR-Polar for other species.

<sup>c</sup> Liu & Macedo for water; He for other species.

combustion of natural gas. The pressure dependencies, relevant for the SCWO conditions were included as well as the collision efficiency of water, when appropriate, using literature values. Troe's formalism [66] was used to derive the modified Arrhenius expressions used at high pressure. Alkam et al. [67] investigated oxidation kinetics of methanol and hydrogen in a supercritical water medium. They suggested that kinetic models developed for low-pressure applications, even the models that contain pressure-dependent reaction rates, should be corrected to account for high-pressure encountered in SCWO conditions. According to this work, the decomposition of  $\text{H}_2\text{O}_2$  into  $\text{OH}^\bullet$  radical is the dominant reaction controlling the destruction of methanol at high pressures, and the reaction rate is twenty times higher than at atmospheric pressure.

Most kinetics found in literature were obtained in flameless conditions and are not able to describe flame regime, predicting slower reaction rates [68]. What is more, these models are not always consistent with each others in the same range of conditions [57,69]. To the best of our knowledge, the only kinetic model adjusted in hydrothermal flame regime is reported by Queiroz et al. [34], developed by adjusting temperature increments in time in order to detect the sharp composition change associated to these temperature changes. Kinetic models could be improved by knowing the concentration of key compounds at different points of reactors especially in hydrothermal flame regime where the reaction rates are faster. Concentration profiles in SCWO reactors are very difficult to obtain due to fast reaction rates and usually only global conversions are reported, except when optical devices are used [70–72]. The lack of reliable kinetic models is one of the reasons why most of the modeling of hydrothermal flames is based on mixing controlled reactions [32,73]. This approach is valid for non-premixed flames at high temperatures since it assumes that chemical reaction is fast compared to the transport processes involved in the flow.

### 3. Hydrothermal flames

Usually a flame is defined as the visible part of the combustion reaction and consists of a surface where reaction occurs. Hydrothermal flames are defined as flames produced in aqueous environments at conditions above the critical point of water ( $P > 22.1$  MPa and  $T > 374^\circ\text{C}$ ) [12]. The flame is a surface which separates the oxidant from the fuel, in the case of diffusion (non-premixed) flames; or it separates the reagents from the reaction products, in case of premixed flames [74]. In premixed flames, that surface is moving towards the reagents with a flame front velocity. If this velocity is the same as the fluid velocity, the flame will remain stationary. If flow velocity is higher or lower than flame front velocity, the flame is blown away from the tube or it will move against the flow, resulting in backfire, respectively [74]. Backfire is a safety problem and must be avoided, and this is usually claimed as a reason for the general preference for non-premixed flames.

The term “hydrothermal combustion” was first used by Franck to describe oxidation processes taking place in dense aqueous environments [11]. The presence of a flame in a SCWO should enhance the elimination efficiency of the SCW medium [75]. However, only a few works about hydrothermal flames have been published [12]. In general, flames ignited spontaneously beyond a certain temperature, normally between 400 and 500 °C [76]. This auto ignition temperature was decreased for higher pressures and fuel concentrations.

The first reactor probably working with a premixed hydrothermal flame inside was the MODAR reactor [33]. Serikawa et al. [77] developed a continuous refrigerated facility for observing hydrothermal flames oxidizing isopropyl alcohol. The ETH Zurich has been developing different continuous hydrothermal

burners working with non premixed flames [78,79]. They used the hydrothermal flame as an internal heat source in a transpiring wall reactor. The direct injection of the waste into a hydrothermal flame was developed as a solution to avoid the external preheating of the feed up to supercritical conditions [78–80]. Sobhy et al. [81] designed a semi-batch visual flame cell, working with methanol-air flames. In the reactors used in the University of Valladolid, operational conditions were above the ignition conditions of IPA according to Serikawa et al. [77], thus they can be described as working at hydrothermal flame regime with a premixed flame [68,82,83]. These reactors present the advantage that the cold feed can be directly injected in the flame without preheating.

SCWO with a hydrothermal flame has a number of advantages over the flameless process. Some of these advantages permit overcoming the traditional challenges that still make difficult the successful and profitable commercialization of SCWO technology [12]:

- It allows the destruction of the organics in residence times of a few milliseconds, which permits the construction of smaller reactors.
- Higher operation temperatures improve the energy recovery.
- It is possible to initiate the reaction with feed injection near to room temperature, avoiding problems such as plugging and corrosion in a preheating system, and having an advantage from the operational and energy integration perspective.

Temperature measurements of hydrothermal flames are presented in Table 3. A direct comparison of experimental data is a not an easy task since singular reactors were used in each set up, some of them including external heating/cooling. In the cases presented in Table 3, visible flames are formed with temperatures around 1000 °C, well below typical temperatures of usual (gaseous) combustion. Steeper et al. [84] found that diffusion flames readily ignite in supercritical mixtures as low as 6 mol% methane or methanol in water, even in the case where fuel concentration is so low that the ignited flame produces no visible light.

Compared to typical reaction temperatures of 450–600 °C in conventional SCWO reactors, hydrothermal flames can reach temperatures above 1000 °C, although bulk temperatures between 600 and 700 °C are normally used. Higher temperatures enable a higher thermodynamic efficiency in the energy recovery, but extraction of hot fluid directly from the hydrothermal flame has significant technical challenges, including corrosion problems. Most reactor designs working in hydrothermal flame regime rely on the injection of coolant streams in order to protect reactor walls from damage caused by the oxidation conditions at such high temperatures [78,80,88]. Such coolant streams dilute the reactor effluent and reduce its thermal quality.

Recently, our research group patented a new cooled wall reactor working with a hydrothermal flame as a heat source that presents the additional advantage that part of the products can be extracted of the reactor by its upper part, without mixing with the cold water, allowing better energy integration because an effluent at temperatures between 600 and 700 °C can be obtained [10].

### 4. Reactors for SCWO

The design of SCWO reactors has evolved on the direction of solving the main problems of the process, as a waste elimination technology without paying attention to the energy integration of the process: corrosion and salt deposition. Thus, besides the largely used tubular reactors, the main developments have been centered on transpiring wall (TWR) and cooled wall reactors (CWR) [89]. These reactors minimize the corrosion by reducing the wall



**Table 3**

Experimental SCWO works with visual observation of hydrothermal flames and temperature measurements.

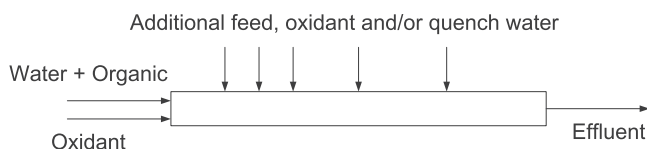
Work	Fuel	Conc.	Oxid. <sup>b</sup> ratio	$T_{ad}$ <sup>a</sup> (°C)	$T_{bulk}$ (°C)	$T_{max}$ (°C)
Příkopský [85]	Methanol	16 wt%	1.3	1465	1100	1200
Serikawa et al. [77]	2-Propanol	6 vol%	2.2	972	580	1100
Sobhy et al. [81]	Methanol	33 vol%	–	1602	590	1100
Sobhy et al. [86]	Methanol	25 vol%	–	1423	–	800
Steeper et al. [84]	Methanol	30 mol%	–	2694	–	1000 <sup>c</sup>
Wellig et al. [80]	Methanol	22 wt%	1.2	1844	1244	–
Zhang et al. [87]	Methanol	35 wt%	1.8	2366	–	900

<sup>a</sup> Theoretical adiabatic reaction temperature calculated with PR-EoS.<sup>b</sup> Missing values correspond to semi-batch experiments, where the equivalence ratio is not defined. Stoichiometric amounts are assumed for those cases.<sup>c</sup> Maximum temperature recordable by the used thermocouple.

temperature. The cooling effect is provided by a flow of water transpiring through a porous wall (TWR) or by a film of cool water (CWR). In any case, temperature of water is usually subcritical, to dissolve the salts, and as a consequence the hot products of oxidation are cooled and diluted, so the outlet temperature of the products is not high enough for a good heat recovery [7]. Due to this, among the many reactors and process modifications developed so far, only a few of them are susceptible to be used if energy production is the main objective of the SCWO facility.

**Tubular reactor.** The tubular reactor is the simplest design and the most used one. Most big and industrial plants constructed so far use this kind of reactor [1]. It has been demonstrated that it is able to sustain hydrothermal flame and complete the reaction in residence times lower than 1 s [68,90], providing a simple and compact device for energy production if “clean” feeds, free of inorganic substances, are used. When dealing with feeds containing inorganic compounds or solids suspension this device presents a series of limitations. Its main disadvantage is the easy plugging of the reactor itself due to precipitation of salts during the oxidation process. To avoid this, the diameters of tubular reactors should be small enough for obtaining a high speed of the circulating fluid in order to reduce the deposition of salts and even then, the precipitated salts can stick to the reactor walls. This lead to another associated problem. Hydrothermal flame presents low flame front propagation velocities, and high flow velocities would make the flame to be blown out of the reactor [83]. Thus, ignition must be produced in every element of the fluid, by preheating feed up to the autoignition temperature of the reaction mixture, which in most cases is around 400 °C. This would lead to serious plugging and corrosion problems also in the preheating system.

Another disadvantage, is the high temperature that the walls of the tube should support (600–700 °C). The whole reactor must be constructed in materials resisting such high temperatures like Ni-alloys. As in this kind of reactors the wall is supporting also the pressure, thick walls of this special materials must be used increasing the cost of reactors. In addition it is possible to suffer the formation of hot spots when oxidation reactions run out of control. A control system discussed in several patents [4] consists of carefully dosing feed, oxidant and/or quenching water through multiple-injection schemes (Fig. 1). This method is a good solution if feed is injected to control the temperature of the reactor as it also allows heating the feeds introduced through the lateral inlets by direct contact with the reaction products, avoiding feed preheating, improving energy integration and avoiding salt precipitation

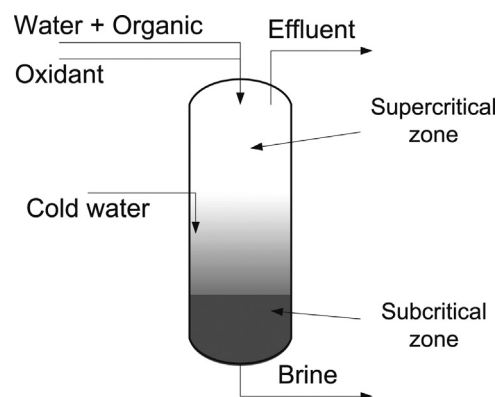
**Fig. 1.** Scheme of tubular reactor.

problems during preheating. On the other hand, quench water injection would highly disfavor energy balance of the facility.

Furthermore, the strategy to periodically wash the equipment with room-temperature water to clean salt deposits, even when having more than one reactor connected in parallel (while one reactor is cleaned the remaining reactors could stay operational) would disfavor tremendously the energy balances. A lot of energy is lost in cooling this heavy thick wall reactors for cleaning and preheating them again for operation.

**Reverse flow tank reactor with a Brine Pool (MODAR Reactor).** This reactor presents a very appropriate design for energy generation and working in hydrothermal flame regime. It consists of an elongated cylinder which constitutes the inner reaction chamber. Inside it there are two different zones: an upper zone at supercritical temperature (near 600 °C), and a lower region at subcritical temperature (~300 °C). The oxidation reaction takes place in the upper zone in which supercritical conditions are achieved. Inorganic salts or other dense material introduced with the feed or formed by chemical reactions are insoluble in supercritical fluids, thus, they precipitate and pass to the subcritical zone where they are dissolved in the brine pool. Furthermore, to avoid the deposition of these substances inside the wall reactor, it has a water film which covers the wall [33]. The upper effluent, free of salts, is available at high temperature, while the salts are retired dissolved in the secondary effluent (brine at subcritical conditions) (Fig. 2).

**Cooled wall reactor.** The cooled wall reactor has a design that separates the effects of temperature and pressure in the SCWO. The external wall, which holds the pressure, is maintained at about 400 °C by the action of a cooling water flow pumped downward between the external and internal walls. This external pressure vessel can be constructed of stainless steel because it is not exposed to oxidizing atmosphere nor temperatures higher than 400 °C. The internal wall is where the reactants are mixed and the reaction takes place. It is built with a special material capable of resist the oxidizing atmosphere at temperatures up to 800 °C [7]. A new

**Fig. 2.** Scheme of MODAR reactor.

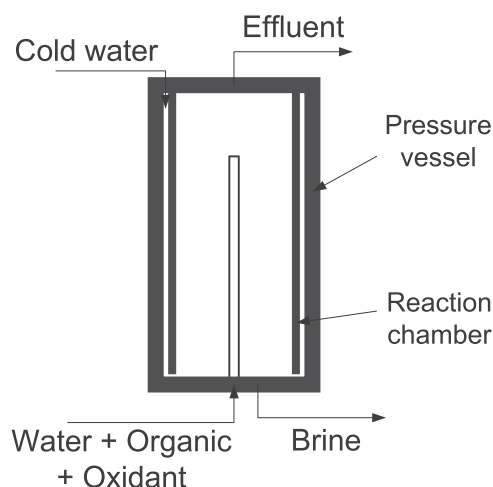


Fig. 3. Scheme of cooled wall reactor.

cooled wall reactor working with a hydrothermal flame as a heat source was patented in 2009 [10]. The main difference compared to previous designs is that aqueous feed and air can be injected cold in the reactor over the hydrothermal flame, while the stream circulating between the pressure vessel and the reaction chamber is simply cold pressurized water. This water stream is entering in the reaction chamber by its lower part, accumulating as a subcritical water “pool” that dissolves the salt precipitated in the upper area of the reactor. It has been tested successfully with salty feeds and with sewage sludge [83,91]. This reactor presents the additional advantage that part of the products can be extracted by its upper part, without mixing with the cold water, allowing better energy integration since an effluent at temperatures between 600 and 700 °C can be obtained (Fig. 3).

The basic concepts given by La Roche et al. [92] for designing these reactors, are still usable; and some specific recommendations for particular reactors can also be found in literature (e.g. [35]).

## 5. SCWO for energy production

The importance of energy recovery (and/or power generation) for successful SCWO commercialization is already highlighted by the interest of SCWO companies in optimizing the energy integration of this processes. SuperWater Solutions claim that their process for sewage sludge oxidation is as efficient generating steam and converting it to electricity as a coal power plant [93]. SuperCritical Fluids International offers as benefit of AquaCritox® process for sludge treatment, the generation of renewable energy by replacing the boiler in a standard steam loop [94].

Basic theoretical calculations indicate that feeds with an energy content of 930 kJ/kg (roughly equivalent to an aqueous solution with 2% (ww) of hexane) can supply enough energy to preheat the feed from room temperature up to 400 °C, and to generate electric power equivalent to that consumed by the high-pressure pump and the air compressor [5]. In practice, higher energy contents are required to achieve an energetically self-sustaining process, due to inefficiencies in the conversion and use of energy.

Vadillo et al. [95] compared some studies, in which technical constraints limit the energy recovery of the process when the outlet temperature of reactors is below 400 °C. In that case, the energy can be recovered by low pressure steam generation or by heating municipal water. They conclude that, from the point of view of power generation, higher temperatures of effluents of SCWO reactor are needed to increase the efficiency of a feasible Rankine cycle. High temperatures at the outlet can only be achieved if the reactor

is designed attending this purpose. The potential of this application is mentioned in some patents [96,97].

Svanström et al. [98] studied the environmental aspects of using SCWO to treat sewage sludge using a life cycle assessment (LCA) methodology. The system studied was the commercial scale plant for sewage sludge from the municipal wastewater treatment facility in Harlingen, TX, USA. They found that gas-fired preheating of the sludge is the major contributor to environmental impacts, and emissions from generating electricity for pumping and for oxygen production are also important. Another conclusion was that an analysis of SCWO processing of sewage sludge is strongly influenced by the system surrounding the actual SCWO unit. This result underscores the necessity to look not only at direct emissions from a specific process, but to investigate the whole life cycle.

One of the key parameters that must be considered for the design of a SCWO system for energy production is the choice of the oxidant. From the reaction point of view, using air or oxygen shows no influence on the conversion of the feed oxidized [40]. Thus, the election of the oxidant is a question of safety and economy, depending on the size of the facility, the energy source available or the working hours. Air is the cheapest material, but it contains a large amount of nitrogen that has to be pressurized, and that acts as a diluent that reduces the temperature of effluents and, therefore, its thermal quality. On the other hand, cryogenic liquid oxygen carries no diluents, and air compressors could be replaced by low consumption cryogenic pumps. Furthermore, pure oxygen does not need to be preheated up to feed injection temperature. However, the cost and energy consumption of producing pure oxygen could affect the viability of the process. For example, Cabeza [9], studied the energy production by SCWO of urban sludge, assuming that the products of reaction could be expanded in a turbine. It was found that, if oxygen is produced in situ by air distillation, the net electricity produced would be positive if the consumption in the distillation process is below 0.99 kWh/kg-O<sub>2</sub>. As reference value, Kansha et al. [99] gives an energetic consumption of 0.40 kWh/kg-O<sub>2</sub>, for a conventional cryogenic plant. An intermediate option is the use of oxygen-enriched air. It is commercially available at different proportions with an oxygen content as high as 95%. Using rich-air with 40% of oxygen, the higher cost of equipment, including compressors and selective membranes for air enrichment, are compensated by moderate electrical cost, since the air flow is nearly half of the corresponding flow of atmospheric air.

Several studies of the production of electrical energy from SCWO has been proposed. Some of them are commented here as function of the global energy production efficiency defined as the electrical energy produced minus the energy consumed divided by the heat content of the waste, as shown in Eq. (1):

$$\text{Global efficiency} = \frac{\text{Produced Power} - \text{Consumed Power}}{\text{Heat of Reaction}} \quad (1)$$

Smith Jr. et al. [14] used exergy analysis to study the partial and total oxidations of methane in supercritical water for a heat-integrated supercritical water reactor and electrical energy production system. They assume a direct expansion of products (at 400 °C) in a turbine, followed by heat recovery of the expanded stream. It was found that the process could be energy self-sufficient and optimum flow rates were calculated in order to minimize reactor heat requirements or maximize net electrical work.

Lavric et al. [6] studied theoretically the energy integration of a SCWO process to treat dilute organic waste at a temperature of 650 °C. Firstly the thermal self-sufficiency is ensured by preheating the feed in a heat exchanger using the hot products. The power self-sufficiency is studied for three possible solutions:

- 1 Supercritical water expansion in a turbine.
- 2 Closed Brayton Cycle.

### 3 Organic Rankine cycle.

Using a small supercritical turbine, the effluent stream at 650 °C is split and 27.5% of the flow is expanded to produce electricity, the remainder being used to preheat the feed. They report a production of 154 kW, enough to cover the consumptions of pump and compressor, with efficiency in producing electricity of 12%. They found that Closed Brayton Cycle with helium or carbon dioxide as working fluids could not even achieve a sufficient production of energy to cover consumption in the process, unless unrealistic efficiencies were assumed for compressors and turbines. In the application of an Organic Rankine Cycle the authors proposed to use the effluent of the reactor at 650 °C to preheat the feed, and using the cooled effluent at 250 °C as a heat source of the Brayton cycle. They found several organic solvents that can be used in the Organic Rankine Cycle covering the power requirements of the plant. The best efficiencies were achieved using R123 as working fluid, and ammonia and isopentane also were suitable choices. The global efficiencies obtained were between 0.15% and 2.6% considering the heat released in the reactor. The results obtained showed that a small scale SCWO plant can be energetically self-sufficient using either a small supercritical turbine or an Organic Rankine Cycle.

Bermejo et al. [100] performed a theoretical study of power generation plant from oxidation of coal by SCWO using a transpiring wall reactor. Two versions of SCWO power plant were proposed. In the first one, the effluent at 650 °C and 30 MPa is expanded in a steam turbine until atmospheric pressure, with an efficiency of 37%. The second alternative of SCWO power plant considers an intermediate reheating for partially expanded steam to get a higher efficiency (40%). It is observed that much higher amount of energy is obtained in this last work than in the work performed by Lavric et al. [6]. In one hand, the objectives of both works are different: in one case it is important to make self-sufficient a small facility, while in the other the viability of a full scale power plant is investigated, thus the solutions adopted in each case are different. In addition, in the second work they make use of an additional fuel to make the preheating of the feed. Even when the calorific power of the additional fuel was taken into account for calculating the global energy efficiency, it is much favorable from the energetic point of view to use this external fuel to preheat the feed than using the effluent. This can be explained because the effluent has a certain amount of energy due to the high pressure that it is lost if the heat content of this stream is used by heat transmission instead of using by expanding in a turbine.

Donatini et al. [15] also discuss the SCWO of coal in power plants with low CO<sub>2</sub> emissions. The power generation system is constituted by a conventional reheat Rankine cycle, using the reactor as boiler (around 600 °C), and an efficiency of 27.9% was found. An innovative application is the use of rotary separator turbines (RST) at depressurization (instead of valves) for recovering part of the pressure work. The RST has the ability to generate power using a two-phase, liquid–vapor stream, while simultaneously separating and pressurizing the liquid in preparation for reinjection. Some conventional applications of RST are geothermal energy systems [101] and refrigeration cycles [102]. However, to the best of our knowledge, practical applications of RST at supercritical pressures are still not reported.

Another analysis was made by Cabeza et al. [91]. In this work, a theoretical analysis of the feasibility of producing energy from the SCWO of sludge was performed. Optimal conditions for the reaction were temperature of 600 °C and pressure of 23 MPa, thus this was considered as the conditions of the effluent. In this work the energy production was considered taking into account different options: direct expansion of the effluent in a supercritical turbine, or generation of steam for a Rankine cycle at 4.6 MPa and 400 °C. Direct

expansion gives an efficiency of 9% with feed at room temperature and preheating the feed with an external heat source improves the process efficiency. Steam generation does not cover the plant demand. However, direct expansion is hampered by higher equipment and operation costs due to harsh operational conditions in the turbine. Another design consideration made in this work is whether reactor feed preheating is carried out by heat exchange with the effluent, or if an external heating system is used. It was found that using an external heat source for feed preheating is more efficient than spending part of effluent energy on it. This result is valid assuming air as oxidant, but have small influence when oxygen is used.

In general, the option of directly expanding the SCWO effluent is, by far, the most energetically efficient. However, it will not be applicable in the short term, mainly due to the fact that the composition of the effluent (50–80% mole of water, carbon dioxide and nitrogen if air is used as oxidant) makes it not suitable for expansion in a conventional turbine, being the effluent an intermediate between the pure water used in steam turbine and the flue gases, products of combustion used in gas turbines. Thus, technical issues prevent the effective implementation of direct expansion in the short term and that is why research is needed in order to develop this energetically more favorable alternative of energy recovery [103].

### 6. Modeling of SCWO

To enhance the development of SCWO processes for industrial-scale applications, including power generation, it is necessary to understand the reactor performance and develop reliable simulation models. Bermejo et al. [104] gave a classification of these models in three main categories. The simplest kind of models assumes some level of conversion (without kinetic modeling) and solves mass and energy balances, like in the works of Cocero et al. [5] and Lavric et al. [105]. This kind of model is useful for analysis of energy efficiency in SCWO, and it just needs accurate values of enthalpies and heat capacities. Increasing complexity, models that include simple flow patterns (plug flow or perfect mixing) can give more information about the behavior of particular reactors (e.g. [19,27,106–108]). Models like those need a kinetic model for the reaction and also good predictions of densities. Due their simplicity they can easily solve non-stationary reactors and can be used in control systems that demands fast responses [108,109]. To overcome the problems of corrosion and salt deposition, and to improve the energy recovery efficiency, several reactors with complex designs have been developed. These reactors can present flow patterns quite different from plug flow or perfectly mixed. Models for these new reactors are also more complicated and usually use CFD tools [18,26,31,32,39]. Thus, this family of models solves conservation equations, the applicable constitutive equations, and dynamically calculates transport properties at different conditions as needed. CFD models can describe temperatures and conversions, show recirculation areas, and predict how the salt deposition occurs. These models are very important when a hydrothermal flame is present or when multiple outlets reactors are used.

When dealing with hydrothermal flames, the turbulence-chemistry interactions become important given the time scale of the processes. The chemical time scale (related to reaction rate) and the mixing time scale (related to turbulence) must be known in order to choose the correct model [110]. In a flameless oxidation, the mixing of reagents is usually faster than the reaction, hence the process is limited by chemistry and an accurate kinetic model is necessary. On the other hand, in presence of a flame, the high temperatures make the reaction rate much higher than the mixing rate, leading to the concept of “mixed is burnt”, where the mixing controls the combustion and a correct mixing model is needed [110].

**Table 4**  
Summary of models of SCWO reactors.

Work	Flow model	System type	Reaction model
Bermejo et al. [26]	CFD	Premixed	Arrhenius
Chen et al. [27]	Plug flow	Premixed	Arrhenius
Donatini et al. [15]	Plug flow	Premixed	— <sup>a</sup>
Dutournié et al. [28]	CFD	Premixed	Arrhenius
Lavric et al. [6]	Plug flow	Premixed	Arrhenius
Leybros et al. [29]	CFD	Premixed	Eddy dissipation
Lieball [18]	CFD	Non-premixed	Arrhenius/Eddy dissipation
Moussi�re et al. [30]	CFD	Premixed	Eddy dissipation
Moussi�re et al. [31]	CFD	Premixed	Eddy dissipation
Narayanan et al. [32]	CFD	Non-premixed	Eddy dissipation
Oh et al. [33]	CFD	Non-premixed	Arrhenius/Eddy dissipation
Queiroz et al. [34]	PFR/CSTR	Premixed	Arrhenius
Queiroz et al. [35]	CFD	Premixed	Arrhenius
Sierra-Pallares et al. [36]	CFD	Non-premixed	Eddy dissipation
Vielca�zals et al. [37]	Plug flow	Premixed <sup>b</sup>	Arrhenius
Zhou et al. [38]	CFD	Premixed	Eddy dissipation
Zhou et al. [39]	CFD	Non-premixed	Arrhenius

<sup>a</sup> Assumes total conversion regardless of kinetic model.<sup>b</sup> It is actually a partially premixed system due the multiple injection of oxygen, but the mixing process is not accounted.

For non-premixed flames, the mixing refers to fuel and oxidant, while for premixed flames, it is related to mixing cold reagents and hot products. In most of CFD works (see Table 4), both characteristic times are calculated and the slowest process is assumed as dominant. Using this approach, Oh et al. [111] identified the zones of their reactor where the reaction is chemistry or mixed controlled. They affirm that the mixing zone downstream of the nozzle where the fluids are mixed is chemical-kinetics limited, and outside of this mixing zone the reaction is diffusion limited. Sierra-Pallares et al. [36] used a mixing model developed for liquid phase, and found better results than the traditional model for gas phase.

Given the importance of turbulence for hydrothermal flames, more developments in turbulence models must be done. Turbulence models are important not only for the mixing description, but also for the heat transfer calculation. The flow in vertical reactors is affected by buoyancy and the heat transfer coefficients can be deteriorated or enhanced, depending on buoyancy forces [112]. Even though there are some studies about the performance of turbulence models for supercritical fluids [73,112–114], there is still not a common opinion about the choice of the turbulence model.

## 7. Research needs and challenges

Oxidation under hydrothermal flame can intensify the supercritical water oxidation process in order to develop micro combustors to produce high pressure and temperature steam from wastes. To develop this process research should be addressed to study the hydrothermal flame oxidation conditions and kinetics of key chemical compounds and wastes. In such applications, feed can be directly introduced in the flame avoiding the highly corrosive preheating step.

Biomass could be also an interesting feed material to produce energy by SCWO with hydrothermal flame as internal heat source. The study of the conditions to produce hydrothermal flame from biomass is a challenge to develop decentralized biorefineries. In addition technical solutions for injecting biomass in a hydrothermal flame combustor must be developed. For example continuously pumping highly concentrated biomass suspensions up to supercritical pressures and its reactor injection is still a challenge.

Different waste and fuels with high concentration in inorganics and heteroatoms, problematic to be burnt with the conventional atmospheric combustion, are potential fuels to be used in SCWO for energy production because, with this technology, clean combustion can be obtained. Nevertheless, inorganics are not soluble in SCW and are susceptible to cause plugging problems in the reactor.

What is more, the introduction of these inert materials in the reactor cause significant energy inefficiency. Research needs to develop SCW pretreatment steps that avoid the introduction of these solids in the SCWO reactor.

Currently, there are a number of reactor designs susceptible to work under hydrothermal flame regime with the main objective of producing energy efficiently such as tubular reactors, reverse flow reactors or cooling wall reactors. Nevertheless their performance in these conditions must be thoroughly investigated and their design and construction materials optimized in order to accomplish this new challenge.

Existing literature on SCWO process focusing on clean energy production has been reviewed. Most of the practical (including commercial) development is based on recovering the heat released by waste oxidation and generating steam. Many theoretical works point that the process would be much more efficient if the compression energy could be recovered as work.

Considering its high temperature and pressure conditions power/shaft work and high grade thermal energy can be potentially recovered from SCWO reactors outlet streams rendering these processes net producers of energy. But those severe conditions, as well as the non-conventional – in the energy-production processes field – composition of streams pose challenges that need to be addressed in order to develop this aspect of the technology. Expansion devices appropriate to streams nature and conditions, and efficient enough should be developed and engineered. This is a major undertaking mainly due to the difficulties related to aero/hydrodynamic, structural and mechanical design concerns. Those will certainly be accompanied by operational issues concerning the handling and mixing of streams at very different pressures and temperatures in common flowpaths, corrosion issues due to particles present in expanding streams, special conditions thermal transfer between streams and dynamic behavior of the energy producing SCWO unit in relation to the plant as a whole in case of tight energy integration.

Modeling is an essential tool to reduce experimental work and to study the scale-up of processes. It becomes even more important when hydrothermal flames are present, since their behavior can not always be observed directly. The improvement of models will require coupling experimental studies with CFD simulations of the reaction process. These models will need better sub-models, especially kinetic, turbulent, and mixture equations of state and transport models. For example, there is still need for transport property methods capable of predicting aqueous mixtures properties in both regions, liquid and supercritical. Also, turbulence models must be validated when applied to supercritical fluids,



where strong variations on thermal and transport properties are expected. Abundant information can be extracted from the supercritical water oxidation previous studies, but there is still space for much more work.

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